Similar improbability attaches to a view which supposes a fluid of such chemical and such morphological characters as the blood of the Lamellibranchiata, to suffer dilution to such an extent as the observable distention of their foot would necessarily imply; and which argues from phenomena noticed on the sudden removal of the animal from the water, as though they could be regarded as identical with normally occurring physiological processes.

As their injections seem to them to prove the existence of a system of vessels distinct from and yet in most close apposition to the blood-vessels, and permeating the several tissues of the body in company with them, the facts of the case seem to the authors to necessitate the belief that a transference of fluid takes place, as in other organisms, from the latter to the former set of vessels.

The animals experimented upon were Unionidæ of the two species, *Anodonta Cygnea* and *Unio margaritifera*.

V. "Notes of Researches on the Poly-Ammonias."—No. XVI. Triatomic Ammonias. By A. W. Hofmann, LL.D., F.R.S. Received July 5, 1861.

In a short paper which I had the honour of submitting to the Royal Society about a year ago, I endeavoured to delineate the general results to which my experiments on the Polyatomic Bases had led me. I showed that the construction of these bodies may be accomplished in two essentially different ways. In the first place, a number of ammonia-molecules may be joined by the insertion of a polyatomic radical, the atomicity of the radical determining the number of the ammonia-molecules thus united.

$$R^n\, Br_n + n\, H_3N = [R^n\, H_{3n}\, N_n]^n\, Br_n.$$

Examples of compounds formed upon this principle have been furnished by my researches on the phosphonias.

Again, the accumulation of the ammonia-molecules may be attempted by increasing the number of polyatomic radicals of given atomicity used as binding material. It is obvious that theoretically any number of ammonia-molecules may be held together by diatomic molecules, provided we appropriately increase the number of the latter.

Diamine.

$$\begin{array}{l} \left.\begin{array}{l}H\\H\\H\end{array}\right\}N \\ \left.\begin{array}{l}H\\H\\H\end{array}\right\}N \end{array} \qquad \left.\begin{array}{l} \left.\begin{array}{l}H\\H\end{array}\right\}N \\ R^{ii} \\ \left.\begin{array}{l}H\\H\end{array}\right\}N \end{array}\right\} = \left.\begin{array}{l}R^{ii}\\H_4\end{array}\right\}N_2.$$

Triamine.

$$\begin{array}{l} \left.\begin{array}{l}H\\H\\H\end{array}\right\}N \\ \left.\begin{array}{l}H\\H\\H\end{array}\right\}N \\ \left.\begin{array}{l}H\\H\\H\end{array}\right\}N \end{array} \qquad \left.\begin{array}{l} \left.\begin{array}{l}H\\H\end{array}\right\}N \\ R^{ii} \\ H\ \}N \\ R^{ii} \\ \left.\begin{array}{l}H\\H\end{array}\right\}N \end{array}\right\} = \left.\begin{array}{l}R_2^{ii}\\H_5\end{array}\right\}N_3.$$

Tetramine.

$$\begin{array}{l} \left.\begin{array}{l}H\\H\\H\end{array}\right\}N \\ \left.\begin{array}{l}H\\H\\H\end{array}\right\}N \\ \left.\begin{array}{l}H\\H\\H\end{array}\right\}N \\ \left.\begin{array}{l}H\\H\\H\end{array}\right\}N \end{array} \qquad \left.\begin{array}{l} \left.\begin{array}{l}H\\H\end{array}\right\}N \\ R^{ii} \\ H\ \}N \\ R^{ii} \\ H\ \}N \\ R^{ii} \\ \left.\begin{array}{l}H\\H\end{array}\right\}N \end{array}\right\} = \left.\begin{array}{l}R_3^{ii}\\H_6\end{array}\right\}N_4.$$

In a general form this second method may be expressed by the equation

$$nR^{ii}Br_2+2n\,H_3N=[R_n^{ii}\,H_{(2n+4)}\,N_{(n+1)}]^{(n+i)}\,Br_{(n+1)}+n-1\,([H_4N]Br),$$

which represents the formation of the first term in each series of a succession of basic groups of increasing atomicity.

The simplest case involved in this equation is the formation of the first term of a series of diammonium-compounds. When $n=1$, the above equation assumes the simple form

$$R^{ii}Br_2+2H_3N=[R^{ii}H_6N_2]^{ii}Br_2\ ;$$

and if $R^{ii}=(C_2H_4)^{ii}$, we obtain in this manner the dibromide of ethylene-diammonium

$$[(C_2H_4)^{ii}H_6N_2]^{ii}Br_2,$$

the diamine of which, undergoing further substitution, furnishes the higher members of this class of diatomic bases.

When $n=2$, the above equation leads us to the conception of the first term of a series of triammonium-compounds, for

$$2R^{ii}Br_2 + 4H_3N = [R_2^{ii}H_8N_3]^{iii}Br_3 + [H_4N]Br;$$

and in attempting the experimental verification of this equation in the ethylene-series, we are justified in expecting, among the products of the action of dibromide of ethylene upon ammonia, the

Tribromide of Diethylene-triammonium. . $[(C_2H_4)_2^{ii}H_8N_3]^{iii}Br_3$,

or among the volatile bases liberated from the bromides by the action of an alkali, the

$$\text{Diethylene-triamine} \quad \left.\begin{matrix}(C_2H_4)_2^{ii}\\ H_5\end{matrix}\right\} N_3,$$

capable, under the continued influence of dibromide of ethylene, of yielding triamines of a higher degree of substitution. These expectations have been fully borne out by experiment. I have satisfied myself that the volatile bases obtained by the action of dibromide of ethylene upon ammonia, which after several rectifications boil between 200° and 220°, consist almost exclusively of the two compounds,

$$\text{Diethylene-triamine } C_4H_{13}N_3 = \left.\begin{matrix}(C_2H_4)_2^{ii}\\ H_5\end{matrix}\right\} N_3, \text{ and}$$

$$\text{Triethylene-triamine } C_6H_{15}N_3 = \left.\begin{matrix}(C_2H_4)_3^{ii}\\ H_3\end{matrix}\right\} N_3.$$

The separation of these two compounds, which, owing to the proximity of their boiling-points, could scarcely be effected by distillation, was attempted by transforming them into saline compounds. But here an unexpected difficulty presented itself in the observation that the triammonias are capable of forming three classes of salts, which may be generally represented as

$$R_2^{ii}H_5N_3,\ 3HCl,$$
$$R_2^{ii}H_5N_3,\ 2HCl,$$
$$R_2^{ii}H_5N_3,\ HCl;$$

and that the platinum-compounds of the triatomic bases exhibit a still greater diversity of composition, these bases being not only apt to form the salts corresponding to the chlorides, viz.—

$$R_2^{ii}H_5N_3,\ 3HCl,\ 3PtCl_2,$$
$$R_2^{ii}H_5N_3,\ 2HCl,\ 2PtCl_2,$$
$$R_2^{ii}H_5N_3,\ HCl,\ PtCl_2,$$

but appearing capable even of forming compounds in which the number of dichloride-of-platinum-molecules diminishes whilst the amount of hydrochloric acid remains constant, such as

$$R_2^{ii} H_5 N_3, 3H Cl, 2Pt Cl_2,$$
$$R_2^{ii} H_5 N_3, 3H Cl, Pt Cl_2.$$

Fortunately most of the salts, and more especially the platinum-compounds, crystallize with remarkable facility, so that the above fact being once established, the circumstances were soon determined under which the more important saline compounds could be with certainty reproduced. The separation of the triamines was chiefly effected in the form of chlorides, bromides, and iodides, or of platinum-salts and gold-salts.

Both diethylene-triamine and triethylene-triamine are powerfully alkaline liquids, soluble in every proportion in water and alcohol, almost insoluble in ether. They boil respectively at 208° and 216°; but owing to the comparatively small quantities with which I have had to work, these determinations may require some slight corrections. Both bases neutralize the acids completely, giving rise to the formation of well-defined, and in most cases beautifully crystallized salts, which are generally very soluble in water, difficultly soluble in alcohol, insoluble in ether. The aqueous solution of the salts is not precipitated by the solutions of the alkalies, owing to the solubility of the bases; but solid hydrate of potassium separates them in the form of nearly colourless oily liquids, which rapidly attract carbonic acid from the atmosphere.

The composition of diethylene-triamine was fixed by the analysis of the free base itself, which was found to be anhydrous,

$$C_4 H_{13} N_3 = \left.\begin{matrix}(C_2 H_4)_2^{ii} \\ H_5\end{matrix}\right\} N_3;$$

and of the triatomic chloride, bromide and iodide, which are all remarkable for the facility and beauty with which they crystallize. These salts contain respectively,—

Trichloride of Diethylene-triammonium	$C_4 H_{16} N_3 Cl_3 = \left[\left.\begin{matrix}(C_2 H_4)_2^{ii} \\ H_8\end{matrix}\right\} N_3\right]^{iii} Cl_3.$
Tribromide of Diethylene-triammonium	$C_4 H_{16} N_3 Br_3 = \left[\left.\begin{matrix}(C_2 H_4)_2^{ii} \\ H_8\end{matrix}\right\} N_3\right]^{ii} Br_3.$
Tri-iodide of Diethylene-triammonium	$C_4 H_{16} N_3 I_3 = \left[\left.\begin{matrix}(C_2 H_4)_2^{ii} \\ H_8\end{matrix}\right\} N_3\right]^{iii} I_3.$

The platinum-salt of diethylene-triamine crystallizes in magnificent golden-yellow needles of the composition

$$C_4H_{16}N_3Pt_3Cl_9 = \left[\left.\begin{matrix}(C_2H_4)_2^{ii}\\ H_8\end{matrix}\right\}N_3\right]^{iii}Cl_3,\ 3PtCl_2.$$

The platinum-salt of this, as well as of several other triammonias which I have examined, cannot be recrystallized without at least partial decomposition. New platinum-compounds are thus produced, in some of which the chloride is united with a smaller number of molecules of dichloride of platinum, whilst others, almost insoluble in water, to judge from the enormous amount of platinum which they contain, appear to be produced by platinic substitution.

Not less definite are the results obtained in the analysis of triethylene-triamine, although, owing to the greater solubility of the compounds of this base and its tendency to form imperfectly saturated salts, the preparation of these substances presents greater difficulties. The analysis of the free base has furnished numbers agreeing with the formula

$$C_6H_{15}N_3 = \left.\begin{matrix}(C_2H_4)_3^{ii}\\ H_3\end{matrix}\right\}N_3,$$

which shows that this, like the diethylenated compound, is anhydrous. It deserves to be noticed that the tendency to form definite hydrates, so prominent in the diamines, is not met with in the case of the triamines.

I have examined numerous salts of triethylene-triamine, both triatomic and diatomic, which confirm the formula of the base. In the presence of a large excess of hydrobromic and hydriodic acids, this substance forms well-crystallized triatomic compounds containing respectively,

Tribromide of Triethylene-triammonium	$C_6H_{18}N_3Br_3 = \left[\left.\begin{matrix}(C_2H_4)_3^{ii}\\ H_6\end{matrix}\right\}N_3\right]^{iii}Br_3,$
Tri-iodide of Triethylene-triammonium	$C_6H_{18}N_3I_3 = \left[\left.\begin{matrix}(C_2H_4)_3^{ii}\\ H_6\end{matrix}\right\}N_3\right]^{iii}I_3.$

The solutions of these salts are powerfully acid.

From feebly acid solutions, on the other hand, salts are deposited in which only two equivalents of hydrobromic or hydriodic acids are present. These substances contain

$$\text{Bromide} \ldots\ldots C_6H_{17}N_3Br_2 = \left.\begin{matrix}(C_2H_4)_3^{ii} \\ H_3\end{matrix}\right\} N_3, 2HBr,$$

$$\text{Iodide} \ldots\ldots C_6H_{17}N_3I_2 = \left.\begin{matrix}(C_2H_4)_3^{ii} \\ H_3\end{matrix}\right\} N_3, 2HI.$$

The addition of free base to the solutions of the diacid salts still further reduces the bromine and iodine. I have not, however, succeeded in obtaining the monacid compounds in a state of purity, but the analysis of mixtures leaves but little doubt regarding the existence of this class, and more especially of the compound

$$C_6H_{16}N_3Br = \left.\begin{matrix}(C_2H_4)_3^{ii} \\ H_3\end{matrix}\right\} N_3, HBr.$$

In addition to the above salts, the triatomic platinum-salt and gold-salt have been submitted to analysis. The former salt contains

$$C_6H_{18}N_3Pt_3Cl_9 = \left[\left.\begin{matrix}(C_2H_4)_3^{ii} \\ H_6\end{matrix}\right\} N_3\right]^{iii} Cl_3, 3PtCl_2.$$

It is one of the finest compounds of the group, crystallizing, as it does, in long golden-coloured needles. They are rather soluble in water, so that the purity of the triethylenated base may be best tested in the form of this platinum-salt, since the platinum-salts of the ethylene-diamines, as well as of diethylene-triamine, with which bases the second triamine is likely to be contaminated, are far less soluble in water. The platinum-salt cannot be recrystallized without suffering decompositions similar to those which alter the salt of the diethylenated triamine. Left in contact with an excess of the corresponding chloride, this platinum-salt undergoes a peculiar metamorphosis. The slender needles, after the lapse of a day or two, are found converted into well-formed prisms of considerable dimensions, containing about 8 per cent. of platinum less than the original compound. The salt appears to be the monatomic platinum-compound,

$$C_6H_{16}N_3PtCl_3 = \left.\begin{matrix}(C_2H_4)_3^{ii} \\ H_3\end{matrix}\right\} N_3, HCl, PtCl_2,$$

although, owing to the transformations which the salt undergoes when treated with water, I have never been able to obtain it in a state of perfect purity.

The gold-salt of triethylene-triamine crystallizes in yellow plates, soluble in water, alcohol, and ether, which contain

$$C_6H_{18}N_3Au_3Cl_{12} = \left[\left.\begin{matrix}(C_2H_4)_3^{ii} \\ H_6\end{matrix}\right\} N_3\right]^{iii} Cl_3, 3AuCl_3.$$

They may be recrystallized from water; only on protracted ebullition they are decomposed with separation of metallic gold.

The triatomic ammonias, the history of which I have endeavoured to trace in this paper, are naturally connected with the triatomic alcohol discovered by Wurtz, and described by him under the name of diethylene-alcohol. Diethylene-triamine and triethylene-triamine occupy in the series of diethylene-alcohol the position which is held by ethylamine and diethylamine, by ethylene-diamine and diethylene-diamine in the series of ethylic and ethylenic alcohols respectively,

$\left.\begin{matrix}(C_2H_5)\\ H\end{matrix}\right\} O$	$\left.\begin{matrix}(C_2H_4)^{ii}\\ H_2\end{matrix}\right\} O_2$	$\left.\begin{matrix}(C_2H_4)_2{}^{ii}\\ H_2\end{matrix}\right\} O_3$
Ethyl-alcohol.	Ethylene-alcohol.	Diethylene-alcohol.
$\left.\begin{matrix}(C_2H_5)\\ H\\ H\end{matrix}\right\} N$	$\left.\begin{matrix}(C_2H_4)^{ii}\\ H_2\\ H_2\end{matrix}\right\} N_2$	$\left.\begin{matrix}(C_2H_4)^{ii}H\\ (C_2H_4)^{ii}H\\ H_3\end{matrix}\right\} N_3$
Ethylamine.	Ethylene-diamine.	Diethylene-triamine.
$\left.\begin{matrix}(C_2H_5)\\ (C_2H_5)\\ H\end{matrix}\right\} N$	$\left.\begin{matrix}(C_2H_4)^{ii}\\ (C_2H_4)^{ii}\\ H_2\end{matrix}\right\} N_2$	$\left.\begin{matrix}(C_2H_4)^{ii}H\\ (C_2H_4)^{ii}H\\ (C_2H_4)^{ii}H\end{matrix}\right\} N_3.$
Diethylamine.	Diethylene-diamine.	Triethylene-triamine.

The above formulæ disclose the perfect symmetry which obtains in the construction of the diatomic and triatomic ammonias; they also show the number and diversity of the ammonias of increasing atomicity.

If the substitution be carried to the furthest limit, viz. to the complete replacement of the hydrogen in the type ammonium, ethylenic substitution in the diatomic derivatives produces *four* compounds, in the same manner as ethylic substitution in ammonium itself. The group of triatomic ethylene-ammoniums does not comprise less than *five* compounds, the last term of the series being a non-volatile body containing *six* molecules of ethylene and represented by the formula

$$C_{12}H_{27}N_3O_3 = \left.\begin{matrix}[(C_2H_4)^{ii}_6 N_3]^{iii}\\ H_3\end{matrix}\right\} O_3,$$

the existence of which is sure to be established experimentally by the continuation of these researches.